Atmospheric
Chemistry
and Physics
Discussions

1 # Variability of polycyclic aromatic hydrocarbons and their
2 # oxidative derivatives in wintertime Beijing, China.

3 Atallah. El zein[1], Rachel Ellen. Dunmore[1], Martyn William. Ward[1], Jacqueline Fiona.
4 Hamilton[1], Alastair Charles. Lewis[2]

5

6 [1]Wolfson Atmospheric Chemistry Laboratories, Department of chemistry, University of York, York, YO10 5DD,
7 United Kingdom
8 [2]National Centre for Atmospheric Science, University of York, York, YO10 5DD, United Kingdom

9 *Correspondence to*: Atallah. El zein (atallah.elzein@york.ac.uk); Alastair C. Lewis (ally.lewis@york.ac.uk)

10 **Abstract.** Ambient particulate matter (PM) can contain a mix of different toxic species derived from a wide
11 variety of sources. This study quantifies the variation in diurnal and nocturnal abundance of 16 Polycyclic
12 Aromatic Hydrocarbons (PAHs), 10 Oxygenated PAHs (OPAHs) and 9 Nitrated PAHs (NPAHs) in ambient PM
13 in central Beijing during winter. Target compounds were identified and quantified using Gas Chromatography –
14 time of flight mass spectrometry (GC-Q-TOF-MS). The total concentration of PAHs varied between 18 and 297
15 ng m^{-3} over 3 h daytime filter samples and from 23 to 165 ng m^{-3} in 15 h night-time samples. The total
16 concentrations of PAHs over 24h varied between 37 and 180 ng m^{-3} (mean: 97 ng m^{-3}). The total daytime
17 concentrations during high particulate loading conditions for PAHs, OPAHs and NPAHs were 224, 54, and 2.3
18 ng m^{-3}, respectively. The most abundant PAHs were fluoranthene (33 ng m^{-3}), chrysene (27 ng m^{-3}), pyrene (27
19 ng m^{-3}), benzo(a)pyrene (27 ng m^{-3}), benzo[b]fluoranthene (25 ng m^{-3}), benzo[a]anthracene (20 ng m^{-3}) and
20 phenanthrene (18 ng m^{-3}). 9,10-Anthraquinone (18 ng m^{-3}), 1,8 Naphthalic anhydride (14 ng m^{-3}) and 9-
21 Fluorenone (12 ng m^{-3}) were the three major OPAHs species, while 9-Nitroanthracene (0.84 ng m^{-3}), 3-
22 Nitrofluoranthene (0.78 ng m^{-3}) and 3-Nitrodibenzofuran (0.45 ng m^{-3}) were the three most abundant NPAHs.
23 ∑PAHs and ∑OPAHs showed a strong positive correlation with the gas phase abundance of NO, CO, SO$_2$, and
24 HONO indicating that PAHs and OPAHs can be associated with both local and regional emissions. Diagnostic
25 ratios suggested emissions from traffic road and coal combustion were the predominant sources for PAHs in
26 Beijing, and also revealed the dominant source of NPAHs was secondary photochemical formation rather than
27 primary emissions. PM$_{2.5}$ and NPAHs showed a strong correlation with gas phase HONO. 9-Nitroanthracene
28 appeared to undergo a photodegradation during the daytime and has shown a strong positive correlation with
29 ambient HONO (R=0.90, P<0.001). The lifetime excess lung cancer risk for the species with available
30 toxicological data (16 PAHs, 1 OPAH and 6 NPAHs) was calculated to be in the range 10^{-5} to 10^{-3} (risk per million
31 people range from 26 to 2053).

32 ## 1 Introduction

33 Outdoor air pollution contains a complex set of toxicological hazards and has become the largest detrimental
34 environmental effect on human health (WHO/IARC., 2016). Exposure to outdoor high particulate loading of PM$_{2.5}$
35 (aerodynamic diameter less than 2.5 µm) is linked to harmful health effects, particularly affecting urban
36 populations (Raaschou et al., 2013; Hamra et al., 2014). The major sources of PM$_{2.5}$ in urban areas are incomplete

Atmospheric
Chemistry
and Physics
Discussions
Open Access
EGU

37   combustion or gas-to-particle conversion, and they contain a varied mix of contaminants including inorganic ions,

38   organic carbon and elemental carbon (Bond et al., 2004; Saikawa et al., 2009). Polycyclic Aromatic Hydrocarbons

39   (PAHs) and their oxidative derivatives (Nitrated PAHs and Oxygenated PAHs) are one class of species with high

40   toxic potency (Zhang et al., 2009; Jia et al., 2011; Wang et al., 2011a). PAHs released in the atmosphere come

41   from both natural and anthropogenic sources; anthropogenic emissions include incomplete combustion of fossil

42   fuels, biomass burning, industrial and agricultural activities and are considered predominant (Zhang et al., 2009;

43   Poulain et al., 2011; Kim et al, 2013; Abbas et al., 2018); natural contributions such as volcanic eruptions and

44   forest fires are reported to be a less significant contributor to total emissions (Xu et al., 2006; Abbas et al, 2018).

45   Vapour phase PAHs can undergo gas phase reaction with oxidants in the atmosphere (e.g. OH radical, ozone and

46   nitrate radicals) leading to the generation of a range of airborne nitrated-PAHs and oxygenated-PAHs (Atkinson

47   et al., 1990; Atkinson and Arey., 1994; Sasaki, 1997). Atmospheric reaction with chlorine atoms in the presence

48   of oxygen has been suggested as a new formation pathway of OPAHs (Riva et al., 2015). Furthermore, OPAHs

49   and NPAHs are often more toxic than the parent PAHs, showing a direct-acting mutagenicity on human cells

50   (Durant et al., 1996; Hannigan et al., 1998; Purohit and Basu, 2000; Wang et al., 2011a; Benbrahim et al., 2012).

51   Beside their formation in the gas phase, OPAHs and NPAHs can also be produced by heterogeneous reactions

52   (Jariyasopit et al., 2014; Zimmermann et al., 2013; Wenyuan et al., 2014; Keyte et al., 2013). Many of these

53   derivatives can also be linked to primary emissions from motor vehicles and combustion processes (Albinet et al.,

54   2007; Shen et al., 2012; Jakober et al., 2007).

55   In recent years, many studies in different countries have focused on studying toxic organic pollutants in $PM_{2.5}$

56   because they lie within the respirable size range for humans (Sharma et al., 2007; Ringuet et al., 2012, Farren et

57   al., 2015). In the last decade, a major focus has been given to Chinese cities because of their population growth

58   and geographic peripheral expansion in manufacturing and energy industries. This has made China the leader in

59   energy consumption, but also the world's highest emitter of $PM_{2.5}$ and PAHs (Lin et al., 2018; Zhang et al., 2009;

60   Xu et al., 2006). The majority of previous studies have reported PAH on 24h $PM_{2.5}$ sampling during short-term

61   and long-term measurements campaigns (Alves et al., 2017; Niu et al., 2017; Benjamin et al., 2014; Wang et al.,

62   2011a). However, a long sampling and averaging period creates some limitations (Tsapakis and Stephanou.,

63   2007), notably where changing atmospheric photolysis conditions (air humidity, temperature, wind direction,

64   ozone or other oxidant concentrations) may have a significant influence on PAHs concentrations and oxidation

65   rates (Tsapakis and Stephanou., 2003; Ringuet et al., 2012). More intensive and higher frequency measurements

66   in field campaigns have been suggested as a means to improve the positive matrix factorization model

67   performance (Tian et al., 2017). A few studies have carried out twice daily (12 h) sampling (Zhang et al., 2018;

68   Farren et al., 2015; Ringuet et al., 2012) obtaining limited information on variability in concentrations during the

69   daytime and night-time (Tsapakis and Stephanou., 2007). Considering the above, this paper determines the

70   temporal diurnal and nocturnal variation of the $PM_{2.5}$-bound concentrations of PAHs, OPAHs and NPAHs from

71   the air of Beijing in China, it shows the role of photochemistry in the formation of OPAHs and NPAHs and

72   associate the fate and evolution of PAHs, OPAHs and NPAHs with the gas phase concentrations of other

73   pollutants (O_3, CO, NO, NO_2, SO_2, HONO), the cancer risk associated with inhalation of $PM_{2.5}$ was calculated.

2 Experimental Steps

2.1 Sampling site and method

The sampling campaign shown in Fig. S1 was located at the Institute of Atmospheric Physics, Chinese Academy of Sciences in Beijing (39°58'28"N 116°22'15"E) as part of the Air Pollution and Human Health (APHH) research programme. $PM_{2.5}$ filter samples were collected on the roof of a 2-storey building about 8m above ground level using a High-Volume Air Sampler (Ecotech HiVol 3000, Victoria, Australia) operating at 1.33 m^3 min^{-1}. Daytime particles were collected every three-hours during high PM concentration levels, nine-hours at low PM levels and over 15 h at night-time during 18 continuous days (22 November 2016 to 9 December 2016). Fifty-seven samples in total were collected. The daytime sampling started at 8:30 in the morning and the filter was changed every 3 h. The night-time period starts at approximately 17:30 until 08:30 the next day. Prior to sampling, the quartz filters (20.3 × 25.4 cm) (supplied by Whatman (Maidstone, U.K.)) were baked at 550 °C for 5 h in order to eliminate any organic matter. After sampling, filters were wrapped in aluminium foil, sealed in polyethylene bags and stored at -20 °C until extraction and analysis.

2.2 Extraction method and clean up

All collected samples were extracted using an Accelerated Solvent Extractor automated system (Dionex, ASE 350). Prior to extraction, 1/16th (surface area equivalent to 25.7 cm^2) of each filter was cut using a hole puncher (Ø=27 mm) and for each batch of 6 samples, one sample was spiked with a mixture of two deuterated-PAHs (Phenanthrene-D10; Pyrene-D10), two deuterated-OPAHs (9-Fluorenone-D8; 9,10-Anthraquinone-D8), and two deuterated-NPAHs (1-Nitronaphthalene-D7; 3-Nitrofluoranthene-D9), as surrogate standards for PAHs, OPAHs and NPAHs, respectively, with concentration on filters corresponding to 400 ng (40 µl, 10 ng $µl^{-1}$ in Acetonitrile). All punched samples were cut to small pieces and packed into 5 mL stainless steel extraction cell. Extractions were carried out in acetonitrile and performed as follows: Oven at 120°C, pressure at 1500 psi, rinse volume 60% and 60 s purge time for three consecutive 5 min cycles. Extracts (V=20ml) were evaporated to approximately 6 mL under a gentle stream of nitrogen before the clean-up step. All samples and blanks were purified on a SPE silica normal phase cartridge (1g/6ml; SIGMA ALDRICH) in order to maintain the GC injection inlet liner. After the clean-up step, the solution of each sample was evaporated to 1 ml under a gentle stream of nitrogen at room temperature (20°C) and transferred to 1.5 ml autosampler amber vial. Each concentrated sample was stored at 4°C until analysis by GC-Q-ToF-MS. The average recovery efficiencies ranged from 85% to 96%, and the target compounds concentrations were calculated incorporating measured recovery efficiencies.

2.3 Chemical standards

The chemical compounds that have attracted the most attention in previous studies are the 16 priority PAHs and their derivatives, defined by the United States Environment Protection Agency (EPA). The choice of the organic compounds investigated in this study is based on those associated with the particle phase and commercially available standards. All compounds are listed in Table 1 and were purchased from Sigma Aldrich, Alfa Aesar and Santa Cruz Biotechnology in the UK and had a minimum purity of 98%. In parallel to individual standards, a

110   mixed solution of the 16 EPA PAHs (CRM47940, Supelco, Sigma Aldrich) of 10 µg ml^{-1} in acetonitrile was also

111   used. Standard solutions for calibrations were prepared in acetonitrile (HPLC grade, 99.9% purity, Sigma

112   Aldrich). Deuterated compounds were supplied by C/D/N isotopes and distributed by QMX Laboratories Ltd

113   (Essex, UK).

114   **2.4 GC/MS Analysis**

115   Target compounds were quantified using a GC - accurate mass Quadrupole Time-of-Flight GC/MS system (GC

116   Agilent 7890B coupled to an Agilent 7200 Q-TOF-MS). Parent PAHs were separated in a 35 min analysis time

117   using a capillary HP-5MS Ultra Inert GC column (Agilent; 5%-Phenyl substituted methylpolysiloxane; length:

118   30 m, diameter: 0.25 mm, film thickness: 0.25 µm). Inlet injections of 1 µl were performed in pulsed splitless

119   mode at 320 °C using an automated liquid injection with the GERSTEL MultiPurpose Sampler (MPS). Helium

120   was used as a carrier gas at 1.4 ml min^{-1}. The GC oven temperature was programmed to 65 °C for 4 min as a

121   starting point and then increased to 185 °C at a heating rate of 40 °C min^{-1} and held for 0.5 min, followed by a

122   heating rate of 10 °C min^{-1} to 240 °C and then ramped at 5 °C min^{-1} until 320 °C and held isothermally for further

123   6 min to ensure all analytes from the extracted samples eluted from the column. The MS was operated in Electron

124   Ionisation (EI) mode at 70 eV with an emission current of 35 µA. Calibration solutions were injected 3 times in

125   the same sequence for samples and covered the range from 1pg µl^{-1} to 1000 pg µl^{-1}.

126   The analysis of OPAHs and NPAHs was conducted using Negative Chemical Ionisation (NCI) performed at 155

127   eV and 48 µA, with methane (CH$_4$, research grade 5.5, Air Liquide) as reagent gas. Target compounds were eluted

128   using the Rxi-5ms (Restek GC column) similar phase and characteristics to HP-5ms. Analysis was performed in

129   29.2 min and the GC settings were selected as follows: 1 µl of each sample was injected in pulsed splitless mode

130   at 310 °C, Helium flow was set to 1.2 ml min^{-1}, the initial oven temperature of 70 °C was held for 4 min, followed

131   by a heating rate of 60 °C min^{-1} until 190 °C and then raised to 270 °C at rate of 25 °C min^{-1} and ended with 5 °C

132   min^{-1} until 320 °C, held for 10 min. A 10 points calibration curve within the concentrations range of 0.5 pg µl^{-1} to

133   1000 pg µl^{-1}, was performed with the correlation coefficients from the linear regression ranging from 0.980 to

134   0.999.

135   **2.5 Data analysis and error evaluation**

136   Data acquisition were recorded and processed using the Agilent Qualitative and Quantitative analysis software.

137   Target compounds were isolated using Extracted-Ion Chromatogram (EIC) and identified by the combination of

138   retention time and mass spectral match against the calibration standards measured simultaneously with the

139   samples. In our study, the limit of detection (LOD) was defined as the valid lowest measurable peak response to

140   peak noise near the elution time of the target peak (S/N = 3) in a mix of standards solutions. As the chemical noise

141   increases during the analysis of real samples the Limit of quantification (LOQ) was defined S/N=10. These

142   recommendations are in accordance with previous analytical studies (Nyiri et al., 2016; Ramírez et al., 2015).

143   LOD values were evaluated from standards solutions and ranged between 1 pg and 20 pg for PAHs, 0.01 pg and

144   0.2 pg (except 1-naphthaldehyde 0.5 pg) for OPAHs and 0.02 pg to 0.25 pg for NPAHs.

145

Atmospheric
Chemistry
and Physics
Discussions

146   We evaluated the precision of the method by calculating the relative standard deviations (%RSD) from replicate

147   analysis as shown in Table 1. For PAHs, the precision of sample replicates (n=10) during interday and intraday

148   varied from 1.8% to 8.9% (mean 5.2%) and 1.2% to 8.7% (mean 3.4%), respectively. The %RSD average for

149   deuterium labelled compounds was about 3.6%. For OPAHs and NPAHs, two different concentrations of

150   standards were analysed (50 pg; n=6 and 400 pg; n=6); interday precision of 10 OPAHs gives an average %RSD

151   of 6.8% (range:5.4-8.9%) and intraday precision of 5.6% (3.2-7.8%). Similar to OPAHs, repeatability and

152   reproducibility between days for NPAHs varied from 3.9% to 8.4% (mean 5.5%) and 3.2% to 9.7% (mean 5.2%),

153   respectively. Hence, the estimated random error quantified by the standard deviation of the measurements did not

154   exceed 7% on average. The systematic error may be due to the influence of the sample matrix during the analysis

155   sequence on the quantification step and the calibration offset. It was estimated to be a maximum 10% from the

156   measured recovery of the deuterium species (Garrido-Frenich et al., 2006). Therefore, the overall estimated

157   uncertainty, combining the precision and the systematic errors, is less than 20%.

158   To determine any sources of contamination during sample preparation and the analytical procedure, the solvent

159   (acetonitrile) and from blank filters were analysed following the same procedure as for the samples (Extraction,

160   SPE, Evaporation). A few target compounds were detected at trace levels but were either below LOD or orders of

161   magnitude lower than in the samples.

162   **3 Results and discussion**

163   **3.1 Temporal variations of PAHs, OPAHs and NPAHs in PM$_{2.5}$**

164   Studies on PM$_{2.5}$ have rapidly increased over the last few years and various disciplines have contributed to improve

165   understanding about source emissions, chemical composition, and impact on people's behaviour and health. The

166   air quality standards in China are currently 35 µg m^{-3} as a yearly average limit for PM$_{2.5}$ and 75 µg m^{-3} as a 24h

167   average limit (WHO 2016; Ministry of Ecology and Environment The People's Republic of China, 2012). During

168   the sampling period of this study (Nov-Dec 2016), PM$_{2.5}$ was measured every hour and ranged from 3.8 to 438 µg

169   m^{-3}, with an average concentration of 103 µg m^{-3}. The average 24h concentration was 108 µg m^{-3} ranging from 10

170   to 283 µg m^{-3}, exceeding the 24h limit value on 10 of the 18 sampling days.

171   Fig. 1 shows the measured concentration of PAHs in the 3 h daytime samples ranging from 18 to 297 ng m^{-3}

172   (average 87.32 ng m^{-3}) and from 23 to 165 ng m^{-3} (average 107.40 ng m^{-3}) in the 15 h night-time samples. The

173   24h total concentrations (combined results from daytime and night-time samples) of the 16 PAHs varied between

174   37 and 180 ng m^{-3} (average 97 ng m^{-3}). PAHs derivatives showed the following trends: total OPAHs

175   concentrations varied from 3.3 to 55 ng.m^{-3} (average: 26 ng m^{-3}) in total daytime hours and from 8.9 to 95 ng m^{-3}

176   (average: 41.63 ng m^{-3}) at night-time; OPAHs were approximately 25 and 14 times higher than average NPAHs

177   in the daytime (average: 1.03 ng m^{-3}, range: 0.13-2.3) and night-time (average: 3.06 ng m^{-3}, range: 0.57-6.43),

178   respectively.

179   PHE (See table 1 for abbreviations), FLT, PYR, BaA, CHR, BbF and BaP were the largest contributors to the

180   total PAHs concentrations, whereas 9-FLON, 9,10-ANQ and 1,8-NANY were the three major O-PAHs species.

181   The most abundant NPAHs were 3-NDBF, 9-NANT and 3-NFLT; contributions of each compound to the total

182   concentration are shown in Fig. 2 and detailed in Table 2. The highest concentrations recorded in this study were

183   in the day of 29 Nov 2016; concentrations of all target compounds in the particulate phase are displayed in Fig.

184   S2. Some nitro-compounds (5-NAC, 1-NPYR, 6-NCHR, 6-NBaP) were below LOQ in few samples while one

185   oxy-compound (1,8-Naphthalic anhydride) was outside the dynamic range and limit of linearity of the calibration

186   curve especially for samples with high mass loading (Table 2). Similar major compounds were found in different

187   urban cities (Xi'an, Jinan, Beijing) of China (Bandowe et al. 2014, Zhang et al. 2018, Wang et al., 2011c). The

188   average of total PAHs concentrations (97 ng m^{-3}) in this study was higher than the average value reported for

189   Guangzhou city in the south of China (average 45.52 ng m^{-3}) (Liu et al., 2015), however, it was lower than average

190   values reported for Xi'an city in winter (range 14-701 ng m^{-3}; average 206 ng m^{-3}) (Wang et al., 2006) and in the

191   suburb of Beijing in winter (average 277 ng m^{-3}) (Feng et al., 2005). The lower average concentration of total

192   PAHs reported in this study can be attributed to the effort from municipal government to improve air quality and

193   control emissions by reducing combustion sources.

194   Concentrations of PAHs in PM$_{10}$ (range: 3.2 - 222.7 ng m^{-3}) in Beijing were found in previous study to be lower

195   than in PM$_{2.5}$ (Wang et al., 2011c). The concentration of PAHs reported in this study were much lower than

196   reported in certain other megacities, for example, Delhi, India in winter season 2003 (range: 948.96-1345.42 ng

197   m^{-3}; mean: 1157.9 ± 113.74 ng m^{-3}) (Sharma et al., 2007) and Mexico City, Mexico in October 2002 (range: 60-

198   910 ng m^{-3}; mean: 310 ng m^{-3}) (Marr et al., 2004). Average concentration for total PAHs in the first 3 h filter of

199   the day (8:30-11:30 am; Monday to Friday; mean: 112 ng m^{-3}) were higher by 1.5 times than the rest of the day,

200   and 1.6 times higher than the same first 3 h on a Sunday. A potential reason of the elevated concentrations in the

201   morning hours is due to the rush hour traffic during working days, probably coupled to a period of shallow

202   boundary layer.

203   The mean total concentrations in Table 2 for the 3 h integration samples of OPAHs and NPAHs were 28.74 ng m^{-3}

204   (range: 1.8 - 87.9 ng m^{-3}) and 1.17 ng m^{-3} (range: 0.15 - 3.92 ng m^{-3}), respectively. Average night-time was 41.63

205   ng m^{-3} (OPAHs) and 3.06 ng m^{-3} (NPAHs), concentrations which were 2.6 and 35 times lower than the average

206   total PAHs in the night samples, respectively. The ratios of mean concentration of PAHs divided by concentration

207   of OPAHs and NPAHs for the 3 h samples were 3.03 and 74, respectively. Ratios of combined daytime and night-

208   time samples (24h) were on average 2.93 (range 1.9 - 4.6) for PAHs/OPAHs and 47.36 (range 25 - 79) for

209   PAHs/NPAHs. Lower ratios were reported from winter study in Xi'an – China, where PAHs/OPAHs ranged from

210   1.75 to 1.86 and PAHs/NPAHs ranged from 34 to 55.2. On the other hand, similar trends to our study were

211   recorded for ∑PAHs/∑OPAHs in Europe such as Athens in Greece in winter (ratio 28.91/6.91 = 4.18) (Andreou

212   and Rapsomanikis., 2009) and Augsburg in Germany in winter (ratio 11/3.2 = 3.43) (Pietrogrande et al., 2011).

213   Further monitoring studies are needed to confirm trends of NPAHs in China.

214   The daily concentration of BaP ranged from 4.46 to 29.8 ng m^{-3} (average 15 ng m^{-3}), exceeding the 24h average

215   limit value of 2.5 ng m^{-3} for China on all of the 18 days of sampling period (Ministry of Ecology and Environment

216   The People's Republic of China, 2012).

217

218 **3.2 Diagnostic ratios to identify emission sources**

219 The concentration ratios between different PAHs are widely used to assess and identify pollution emission sources
220 (Tobiszewski and Namieśnik., 2012 and references therein). The ratios of FLT/(FLT + PYR) and IcdP/(IcdP +
221 BghiP) isomer pairs are commonly used to distinguish emission sources such as coal/biomass burning or the
222 incomplete combustion of petroleum. Values of FLT/(FLT + PYR) and IcdP/(IcdP + BghiP) higher than 0.5
223 indicate dominance of a coal/biomass burning source. Values of FLT/(FLT + PYR) between 0.4 and 0.5 and
224 IcdP/(IcdP + BghiP) between 0.2 and 0.5 suggest a higher influence from fossil fuel combustion; values less than
225 0.4 and 0.2, are mostly related to incomplete combustion (petrogenic origin) (Yunker et al., 2002; Pio et al., 2001).
226 The measured ratios in this study are shown in Fig. 3 and ranged from 0.53 to 0.67 (mean 0.56) during the day (3
227 h and 9 h samples), while at night (15 h samples) varied between 0.51 and 0.54 (mean 0.52) indicating primary
228 emissions from coal and biomass burning. Lower values were observed for IcdP/(IcdP + BghiP) where daytime
229 ratios were between 0.39 and 0.5 (3 h and 9 h samples) indicating the dominance of petroleum combustion. At
230 night, the ratio in most samples was slightly higher than 0.5, with some values below, suggesting mixed sources
231 with likley higher contributions coming from residential heating using coal and wood at night.

232 Other ratios can be useful to confirm the contribution from local traffic and to discriminate vehicle emissions such
233 as BaP/BghiP, FLU/FLU+PYR and BaP/BaP+CHR (Tobiszewski and Namieśnik., 2012 and references therein).
234 The BaP/BghiP ratios were significantly higher than 0.6 indicating a major influence from road traffic, while
235 FLU/FLU+PYR ratios suggested a predominant petrol contribution (ratio < 0.5) instead of diesel engines (ratio >
236 0.5). Results shown in Fig. 4 identify **traffic emissions and in particular petrol engines** as the major emitter of
237 PAHs. In $PM_{2.5}$, the 5- and 6-rings PAHs species (BaP, IcdP, BghiP) were previously attributed to petrol engines,
238 while lower molecular weight with 3-rings (ACY, AC, FLU, PHE, ANT) and 4-rings (FLT, PYR, BaA, CHR)
239 were closely related to diesel vehicle emissions (Chiang et al., 2012; Wu et al., 2014 and references therein).
240 Previous studies in Beijing and Guangzhou in China suggested similar contributions from coal and petroleum
241 combustion, focusing on vehicular traffic (petrol and diesel) as potential sources for PAHs (Gao and Ji., 2018;
242 Liu et al., 2015; Wu et al., 2014, Niu et al., 2017).

243 On the other hand, some NPAHs can be used to track the photochemistry of PAHs with OH and NO_3 radicals,
244 both of which can generate secondary photochemical products of NPAHs and OPAHs from primary PAH
245 emissions (Zhang et al., 2018; Ringuet et al., 2012; Wang et al., 2011a). As 1-NPYR originates mainly from
246 primary emissions and in particular from diesel vehicles (Ringuet et al., 2012 and references therein), formation
247 of 2-NFLT has been reported to be absent in direct combustion emissions and to be produced from the gas-phase
248 reactions of FLT with OH radicals in presence of NOx during the day or NO_3 radicals at night; while 2-NPYR
249 comes solely from the reaction of PYR with OH radicals (Ramdahl et al., 1986; Arey et al., 1986; Atkinson et al.,
250 1987; Ciccioli et al., 1996). Accordingly, the ratio 2-NFLT/1-NPYR has been widely used, with a value greater
251 than 5 indicating a major contribution from photochemical processes, whilst a ratio value less than 5 means an
252 important contribution from direct emissions (Zhang et al., 2018; Bandowe et al., 2014; Ringuet et al., 2012;
253 Wang et al., 2011a; Albinet et al., 2008).

254 In this study, the 2-NFLT was not quantified because the standard compound was not commercially available,
255 subsequently, we have used 3-NFLT isomer as a substitution of 2-NFLT. A previous study reported that the

256 concentration of 3-NFLT compared to 2-NFLT is relatively very low (Bamford et al., 2003); in addition, the

257 separation of both isomers (2- and 3-NFLT) using the most common GC-MS column for PAHs separation, HP-

258 5ms and DB-5ms, was not possible (Zhang et al., 2018; Bandowe et al., 2014; Ringuet et al., 2012; Albinet et al.,

259 2008). Hence, in this study we assume that the sum of 2- and 3-NFLT is closely representative of the original ratio

260 2-NFLT/1-NPYR. Therefore, we adopted the ratio 2+3NFLT/1-NPYR which was varied between 4 and 19 during

261 the daytime (mean: 12) and from 3.6 to 30.4 in the night-time (mean: 8.8) (Fig. S3). Most daytime values have

262 exceeded significantly the benchmark ratio of 5, while at night-time the average value was lower than average

263 daytime value. These results could illustrate the predominance of OH-radicals-initiated reaction during the day

264 and the dominating atmospheric formation route for 2-NFLT in presence of NO_2 and sunlight.

265

266 **3.3 Correlation with atmospheric gas pollutants**

267 The O_3, CO, NO, NO_2, SO_2 and HONO concentrations were also measured at the same site location (Institute of

268 Atmospheric Physics in Beijing) as the $PM_{2.5}$ sampling. Sampling inlets were installed outside the containers at

269 approximately 3-4 m above ground (Fig. S1). Online measurements of the gas phase species have been time-

270 averaged to the filter sampling times. No correlations of significance were seen between PAHs and meteorological

271 parameters (Relative Humidity and Temperature).

272 ∑PAHs and ∑OPAHs had a similar strong positive correlation (R= 0.82 to 0.98) in the 9 h and 15 h samples with

273 CO, NO, NO_2, SO_2 and HONO (Table S1). NO is known as an effective tracer for local traffic emissions, it is a

274 short-lived intermediate in a variety of chemical reactions in both the troposphere and the stratosphere with an

275 approximate residence time of 1 day (Bange 2008, Janhäll et al., 2004). CO is mainly produced from incomplete

276 combustion and has a relatively long atmospheric lifetime (3 months on average) and has been reported to undergo

277 long-range transport (Peng et al., 2007 and references therein). This suggests that the observed high correlations

278 with primary pollutants NO and CO during the daytime and night-time indicate that PAHs and OPAHs are

279 primarily emitted from traffic and can be associated with both local and regional scale emissions. In addition,

280 similar significant correlations were observed with SO_2, this gas is mostly emitted from power plants emissions

281 outside the city with approximately 50 h (Lee et al., 2011) atmospheric residence time. This relationship could be

282 explained by the contribution of anthropogenic sources such as the Beijing Taiyanggong thermal power station

283 (39°58′42″N 116°26′19″E). This suggestion is in accordance with our measured air masses showing that winds

284 arriving at the site blow from the North East for much of the time (Fig. S4).

285 In contrast, most of the 3 h day samples showed only moderate correlations (R=0.38 to 0.74) except for HONO

286 where significant correlations (R=0.87 to 0.94) were observed with ∑PAHs, ∑OPAHs and ∑NPAHs (Fig. 5;

287 Table S1). Furthermore, HONO was significantly correlated with $PM_{2.5}$ during the daytime (Fig. 5). In light with

288 these findings, a strong chemical link between HONO emissions and ambient particles ($PM_{2.5}$) can be concluded.

289 A similar conclusion was drawn from recent study in Beijing (Zhang et al., 2019) which suggested a potential

290 chemical relationship between HONO and haze particles ($PM_{2.5}$) and proposed a high contribution from vehicle

291 emissions to the night-time HONO.

Atmospheric
Chemistry
and Physics
Discussions

292 For NPAHs, no significant correlation was found in 3 h and 15 h time sampling resolution, except with HONO,
293 where a significant difference between day and night were observed. Surprisingly, the 9 h time resolution showed
294 a strong correlation with CO, NO, NO_2 and SO_2, potentially suggesting a direct emission of NPAHs. More likely
295 these correlations arise because of a formation delay of NPAHs that is smoothed out by the longer daytime
296 sampling period. In a previous study, Zimmermann et al., (2013) reported the formation of NPAHs from the
297 heterogeneous interaction of ambient particle bound-PAHs with atmospheric oxidant. In line with the observed
298 high values for the ratio 2+3NFLT/1-NPYR (section 3.2) and the trace levels of NPAHs concentrations in the
299 atmosphere; the secondary formation of NPAHs by gas phase reactions followed by adsorption on particles and
300 in parallel the heterogeneous formation on the surface of particles is supported rather than primary emissions.

301 HONO plays a key role in tropospheric photochemistry, however its sources and their relative contributions to
302 ambient HONO are still unclear, especially in the daytime. To help understand the mechanism of HONO
303 formation in the atmosphere, each NPAHs compound has been correlated with HONO concentrations. The
304 available data in Table S2 shows diurnal and nocturnal differences for individual correlation of NPAHs with
305 HONO with the exception for 1-NPYR, which originates mainly from primary emissions and shows a strong
306 correlation during the day and night. In addition, 9-Nitroanthracene had distinctive behaviour by accumulating
307 during the night and appearing to undergo a photodegradation during the daytime (Fig. 6). 9-Nitroanthracene
308 showed a strong positive correlation with HONO (R=0.90, P<0.001) in the daytime while no significant
309 relationship was found at night-time (R=0.15, P>0.05). This suggests 9-nitroanthracene as a possible source of
310 HONO during the daytime via the OH radical-initiated reaction leading to OH (Ortho) addition and followed by
311 intramolecular hydrogen transfer from the phenolic hydroxyl group to the nitro group.

312 In addition, there was a significant positive correlation between ANT and 9-NANT (R= 0.90, 1/3 h; R=0.94, 1/9
313 h; R=0.90, 1/15 h; P≤0.001), which may be an indication that 9-NANT is closely related to ANT. In this respect,
314 additional simulation chamber measurements of the gas phase reaction of ANT with NO_3 radicals and for 9-
315 Nitroanthracene with OH radicals in presence of light and under different atmospheric parameters are required for
316 more precise assessment.

317

318 **3.4 Exposure assessment**

319 The toxicity equivalency factor (TEF) represent an estimate of the relative toxicity of a chemical compared to a
320 reference chemical. For PAHs, Benzo(a)pyrene was chosen as the reference chemical because it is known as the
321 most carcinogenic PAH (OEHHA., 1994, 2002) and is commonly used as an indicator of carcinogenicity of total
322 PAHs (Alves et al., 2017; Bandowe et al., 2014; Ramírez et al., 2011). The toxicity of the total PAHs expressed
323 as BaP equivalents (BaP_{eq}) is calculated from the TEFs of each target compound (Table S3) multiplied by its
324 corresponding concentration Eq. (1):

325
$$\sum [BaP]_{eq} = \sum_{i}^{n=1} (C_i \; x \; TEF_i) \qquad (1)$$

326 where C_i correspond to the concentration of individual target compound (PAHs, OPAHs and NPAHs) in ng m^{-3}.

Atmospheric
Chemistry
and Physics
Discussions

327

328   A widely applied procedure of the Office of Environmental Health Hazards Assessment (OEHHA) of the

329   California Environmental Protection Agency (CalEPA) and the World Health Organisation (WHO) was used in

330   this study to evaluate and calculate the potential of contracting cancer from inhalation and exposure to $PM_{2.5}$-

331   bound PAHs; commonly known as the lifetime excess cancer risk (ECR) Eq. (2).

332
$$ECR = \sum [BaP]_{eq} \times UR_{BaP} \qquad (2)$$

333   where two values are mostly used for $UR_{[BaP]}$ (1.1×10^{-6} (ng m^{-3})$^{-1}$ (OEHHA., 2002, 2005) and 8.7×10^{-5} (ng m^{-3})$^{-1}$

334   (WHO., 2000)); Eq. (2) describes the inhalation unit risk associated with high probability of contracting cancer

335   when exposed continuously to 1 ng m^{-3} of BaP_{eq} concentration over a lifetime of 70 years.

336   As shown in Table 3, the BaP_{eq} concentrations include the sum of 16PAHs, 1OPAH and 6NPAHs, and the cancer

337   risk was evaluated among different sampling times according to CalEPA and WHO guidelines. The risk values

338   may be underestimated due to lack of toxicity data for OPAHs and because our assessment excludes the gas phase

339   contributions and are only based on the health risk evaluation of particulate phase. The average 24h BaP_{eq} for the

340   whole sampling period was 23.6 ng m^{-3}. 6-NCHR has not been quantified in all samples, its contribution to the

341   total BaP_{eq} is relatively high (mean: 8%, range: 1-24%) in comparison with the three major contributor from the

342   PAH group: BaP (mean: 47.5%, range: 24-64%), DahA (mean: 17.8%, range: 10-32%) and BbF (mean: 10.1%,

343   range: 7-21%). In this study, the ECR attributable to polycyclic aromatic compounds (PACs) in urban air of

344   Beijing ranged from 10^{-5} to $10^{-3} > 10^{-6}$ suggesting a high potential cancer risk for adults (Chen and Liao., 2006;

345   Bai et al., 2009).

346   It is worth noting that inhalation exposure is not the only risk with the potential to contract cancer to humans,

347   other sources of exposure such as dermal contact and ingestion of the re-suspended dusts in real environmental

348   matrices such as road dusts and soils could increase the risk value for urban residents (Wang, et al., 2011b; Wei

349   et al., 2015). In our study, the 24h average estimated cancer risk from inhalation exposure to ambient $PM_{2.5}$ based

350   on CalEPA and WHO guidelines were 2.6×10^{-5} and 2.05×10^{-3}, respectively. Hence, the highest calculated ECR

351   (2.05×10^{-3}) estimates 2027 additional cases per million people exposed (29 cases/year) in comparison to the

352   estimate based on CalEPA in which 26 persons (0.37 cases/year) may have a chance of cancer development.

353   ECR trends were reported in previous studies from Beijing and other populated area (Bandowe et al., 2014; Alves

354   et al., 2017; Ramírez et al., 2011; Jia et al., 2011, Liu et al., 2015, Feng et al., 2018, Song et al., 2018). In this

355   study we considered the combination of all samples (n=54) to estimate the average 24h cancer risk ($\sum[BaP]_{eq}$=23.6

356   ± 12 ng m^{-3}; range 8 – 44 ng m^{-3}) and compare it with previous studies. An average value of 17 ng m^{-3} (range 2-

357   64 ng m^{-3}) was reported for Xi'an for the whole year between July 2008 and August 2009 (Bandowe et al., 2014).

358   After considering the same winter period (November and December) as in our study, the average values reported

359   for Xi'an city (31-33 ng m^{-3}) were higher than our results. In contrast, our average value was comparable to those

360   reported in a recent study in Beijing, ranging from 21 to 38 ng m^{-3} in cold months (Feng et al., 2018), whilst in

361   the previous study of Chen et al. 2017, they reported an average of 31.4 ng m^{-3} for outdoor air in Beijing in winter.

362   Lower and more varied values have been also reported to Beijing city in winter. Liu et al. (2007) reported an

363   average BaP_{eq} concentration of 13.0 ng m^{-3} and 27.3 ng m^{-3} at two sampling sites on Peking University campus

Atmospheric
Chemistry
and Physics
Discussions

364   and 82.1 ng m^{-3} for samples collected from busy road street. It is clear that direct comparison with Beijing air

365   from other studies can be limited due to the number of PACs considered in each study and the differences in

366   sampling sites and sampling periods. Other areas of uncertainty include TEF reference values and the range of

367   BaP UR which were extrapolated from animal bioassays with limited evidence regarding the carcinogenicity to

368   humans.

369   Seasonal variability is also crucial in estimating BaP$_{eq}$ concentrations; it has been shown that BaP$_{eq}$ values in cold

370   months are always higher than warm months due to the increase in coal combustion, central and residential

371   heating, lower photochemical transformation and lower volatilisation of gases favorising particle formation in

372   winter. Previous observations in Beijing recorded ∑[BaP$_{eq}$] of 11.1 ng m^{-3} in autumn (Jia et al., 2011) and 11.0

373   ng m^{-3} in warm months (April to June) (Feng et al., 2018). In comparison with Guangzhou city (south of China),

374   BaP$_{eq}$ was 9.24 ng m^{-3} in winter and reported to be 1.6 and 6.2 times greater than autumn and summer, respectively

375   (Liu et al., 2015). Our results were considerably higher than those estimated for western European cities during

376   the winter, such as Oporto: 3.56 ng m^{-3}, Florence: 1.39 ng m^{-3} and Athens: 0.43 ng m^{-3} (Alves et al., 2017). ECR

377   values estimated for each city were 6.6, 17 and 55 times lower than our ECR estimation. Lower ECR levels in

378   western European cities were attributed to cleaner and renewable energy sources, less populated cities, waste

379   exports and recycling and more efficient environmental regulations.

380

381   4 Conclusions

382   Temporal variations and chemical composition of PM$_{2.5}$ were measured in Beijing-China from 22 November 2016

383   to 9 December 2016, focusing in particularly on the diurnal and nocturnal chemical formation of PAHs, OPAH

384   and NPAHs. The 24h average concentration of PM$_{2.5}$ was 108 µg m^{-3} ranging from 10 to 283 µg m^{-3}, exceeding

385   the 24h limit for China on 10 days of the 18 sampling days. The 24h concentrations of ∑PAH$_{16}$ varied between

386   37 and 180 ng m^{-3} (average 97 ng m^{-3}), while ∑OPAH$_{10}$ ranged from 13 to 70 ng m^{-3} (average 35.62 ng m^{-3}) and

387   ∑NPAH$_9$ from 0.87 to 4.4 ng m^{-3} (average 2.29 ng m^{-3}). Daytime concentrations during pollution episodes for

388   PAHs, OPAHs and NPAHs were 224, 54, and 2.3 ng m^{-3}, respectively. The daily concentration of BaP exceeded

389   the 24h average limit of 2.5 ng m^{-3} for China on all sampling days in this study, indicating elevated risk of disease

390   among inhabitants.

391   Diagnostic ratios of different species were used to distinguish between possible emission sources of PAHs. Coal

392   combustion and road traffic emissions (petrol engines) were found overall to be the two dominant sources. In

393   addition, the high ratios of 2+3NFLT/1-NPYR observed reveal the significance of secondary formation of

394   NPAHs, especially in daytime, and the dominance of the OH radical-initiated reaction pathway.

395   PAHs and OPAHs concentrations were correlated with CO, NO, NO$_2$, SO$_2$ and HONO, indicating that these

396   compounds can be associated with both local and regional primary emissions and mostly related to traffic

397   contribution. Correlation between PM$_{2.5}$ and HONO suggested a possible link with PM$_{2.5}$ as a potential source of

398   HONO, affecting the tropospheric budget of HONO and OH radicals. The strong positive correlation between

399   individual NPAHs and HONO during daytime was also suggestive of a potential link between these two classes

400 of chemicals in air. One of the dominant NPAHs, the 9-NANT had a distinctive behaviour, accumulating at night

401 and photodegrading in daytime.

402 The lifetime excess cancer risk attributable to the summation of polycyclic aromatic compounds measured here

403 and associated with $PM_{2.5}$ inhalations in Beijing was in the range of 10^{-3} according to WHO guidelines, confirming

404 that there is statistically elevated risk of contracting cancer from this class of pollutants in this location.

405

406

407 *Author contributions:* AE led the analysis and prepared the manuscript with contributions from all authors. ACL

408 and JFH contributed to the analysis, interpretation and writing of the paper. RED provided the data on the gas

409 phase measurements and collected the filter samples in the field. MWW supported laboratory chemical analysis

410 on the GC-Q/ToF-MS. All authors contributed to the corrections of the paper.

411

412 *Competing interests.* The authors declare that they have no competing interests.

413

419
420

Atmospheric
Chemistry
and Physics
Discussions

421   **References**

422   Albinet, A., Leoz-Garziandia, E., Budzinski, H., Villenave, E.: Polycyclic aromatic hydrocarbons (PAHs), nitrated

423   PAHs and oxygenated PAHs in ambient air of the Marseilles area (South of France): Concentrations and sources,

424   Science. of the Total. Environment., 384, 280–292, doi:10.1016/j.scitotenv.2007.04.028, 2007.

425   Albinet, A., Leoz-Garziandia, E., Budzinski, H., Villenave, E., Jaffrezo, J. L.: Nitrated and oxygenated derivatives

426   of polycyclic aromatic hydrocarbons in the ambient air of two French alpine valleys Part 1: Concentrations,

427   sources   and   gas/particle   partitioning,   Atmospheric.   Environment.   42,   43–54,

428   doi:10.1016/j.atmosenv.2007.10.009, 2008.

429   Abbas, I., Badran, G., Verdin, A., Ledoux, F., Roumie, M., Courcot, D.: Polycyclic aromatic hydrocarbon

430   derivatives in airborne particulate matter: sources, analysis and toxicity, Environmental. Chemistry. Letters., 16,

431   439-475   doi.org/10.1007/s10311-017-0697-0, 2018.

432   Alves, C. A., Vicente, A. M., Custódio, D., Cerqueira, M., et al.: Polycyclic aromatic hydrocarbons and their

433   derivatives (nitro-PAHs, oxygenated PAHs, and azaarenes) in $PM_{2.5}$ from Southern European cities, Science. of

434   the Total. Environment. 595, 494–504, doi:10.1016/j.scitotenv.2017.03.256, 2017.

435   Atkinson, R., and Arey, J.: Atmospheric chemistry of gas-phase polycyclic aromatic hydrocarbons: formation of

436   atmospheric mutagens, Environ. Health. Perspect., 102, 117–126, 1994.

437   Atkinson, R., Arey, J., Zielinska, B., Aschmann, S. M.: Kinetics and nitro-products of the gas-phase OH and NO_3

438   radical-initiated reactions of naphthalene-d8, fluoranthene-d10, and pyrene, Int. J. Chem. Kinet., 22, 999–1014,

439   1990.

440   Atkinson, R., Arey, J., Zielinska, B., Pitts Jr, J.N., Winer, A.M.: Evidence for the transformation of polycyclic

441   organic matter in the atmosphere, Atmospheric. Environment., 21, 2261–2262, doi:10.1016/0004-

442   6981(87)90357-X, 1987.

443   Andreou, G., Rapsomanikis. S.: Polycyclic aromatic hydrocarbons and their oxygenated derivatives in the urban

444   atmosphere of Athens, Journal. of Hazardous. Materials., 172, 363–373, doi:10.1016/j.jhazmat.2009.07.023,

445   2009.

446   Arey, J., Zielinska, B., Atkinson, R., Winer, A. M., Ramdahl, T., Pitts Jr, J. N.: The formation of nitro-PAH from

447   the gas-phase reactions of fluoranthene and pyrene with the OH radical in the presence of NO_x, Atmospheric.

448   Environment., 20, 2339-2345, doi: 10.1016/0004-6981(86)90064-8, 1986.

449   Bond, T. C., Streets, D. G., Yarber, K. F., Nelson, S. M., Woo, J. H., Klimont, Z.: A technology-based global

450   inventory of black and organic carbon emissions from combustion, J. Geophys. Res., 109, D14203,

451   doi:10.1029/2003JD003697, 2004.

452   Bandowe, B.A.M., Meusel, H., Huang, R. J., Ho, K., Cao, J., Hoffmann, T., Wilcke, W.: $PM_{2.5}$-bound oxygenated

453   PAHs, nitro-PAHs and parent-PAHs from the atmosphere of a Chinese megacity: Seasonal variation, sources and

454   cancer   risk   assessment,   Science.   of   the   Total.   Environment.,   473–474,   77–87,   doi:

455   10.1016/j.scitotenv.2013.11.108, 2014.

Atmospheric
Chemistry
and Physics
Discussions

456 Benbrahim-Tallaa, L., Baan, R. A., Grosse, Y., Lauby-Secretan, B., El Ghissassi, F., Bouvard, V., et al.:
457 Carcinogenicity of diesel-engine and gasoline-engine exhausts and some nitroarenes, Lancet. Oncol., 13, 663–
458 664, doi:10.1016/S1470-2045(12)70280-2, 2012.

459 Bai, Z., Hu, Y., Yu, H., Wu, N., You, Y.: Quantitative health risk assessment of inhalation exposure to polycyclic
460 aromatic hydrocarbons on citizens in Tianjin, China. Bull. Environ. Contam. Toxicol. 83, 151–154, doi:
461 10.1007/s00128-009-9686-8, 2009.

462 Bamford, H. A. and Baker, J. E.: Nitro-polycyclic aromatic hydrocarbon concentrations and sources in urban and
463 suburban atmospheres of the Mid-Atlantic region. Atmospheric. Environment., 37, 2077–2091.
464 doi:10.1016/S1352-2310(03)00102-X, 2003.

465 Bange, H.: Chapter 2 - Gaseous Nitrogen Compounds (NO, N_2O, N_2, NH_3) in the Ocean in Nitrogen in the Marine
466 Environment (Second Edition), 51-94, 2008.

467 Chen, S.C. and Liao, C.M.: Health risk assessment on human exposed to environmental polycyclic aromatic
468 hydrocarbons pollution sources, Science. of the Total. Environment. 366, 112–123,
469 doi:10.1016/j.scitotenv.2005.08.047, 2006.

470 Chen, Y., Li, X., Zhu, T., Han, Y., Lv, D.: PM2.5-bound PAHs in three indoor and one outdoor air in Beijing:
471 Concentration, source and health risk assessment, Science of the Total Environment 586, 255–264,
472 doi:10.1016/j.scitotenv.2017.01.214, 2017.

473 Chiang, H.L., Lai, Y.M., Chang, S.Y.: Pollutant constituents of exhaust emitted from light-duty diesel vehicles,
474 Atmospheric. Environment. 47, 399-406, doi:10.1016/j.atmosenv.2011.10.045, 2012.

475 Ciccioli, P., Cecinato, A., Brancaleoni, E., Frattoni, M., Zacchei, P., Miguel, A.H.: Formation and transport of 2-
476 nitrofluoranthene and 2-nitropyrene of photochemical origin in the troposphere, J. Geophys. Res., 101, 19567–
477 19581, doi: 10.1029/95JD02118, 1996.

478 Durant, J.L., Busby Jr, W.F., Lafleur, A.L., Penman, B.W., Crespi, C.L.: Human cell mutagenicity of oxygenated,
479 nitrated and unsubstituted polycyclic aromatic hydrocarbons associated with urban aerosols, Mutat. Res. Genet.
480 Toxicol., 371, 123-157, doi:10.1016/S0165-1218(96)90103-2, 1996.

481 Farren, N.J., Ramírez, N., Lee, J.D., Finessi, E., Lewis, A.C., Hamilton, J.F.: Estimated Exposure Risks from
482 Carcinogenic Nitrosamines in Urban Airborne Particulate Matter, Environ. Sci. Technol., 49, 9648−9656, doi:
483 10.1021/acs.est.5b01620, 2015.

484 Feng, B., Li, L., Xu, H., Wang, T, Wu, R., Chen, J., Zhang, Y., Liu, S., Ho, S.S.H., Cao, J., Huang, W.: $PM_{2.5}$-
485 bound polycyclic aromatic hydrocarbons (PAHs) in Beijing: Seasonal variations, sources, and risk assessment,
486 Journal. of Environmental. Sciences., 77, 11-19, doi:10.1016/j.jes.2017.12.025, 2018.

487 Feng, J., Chan, C. K., Fang, M., Hu, M., He, L., Tang, X.: Impact of meteorology and energy structure on solvent
488 extractable organic compounds of $PM_{2.5}$ in Beijing, China, Chemosphere. 61, 623–632,
489 doi:10.1016/j.chemosphere.2005.03.067, 2005.

490   Garrido-Frenich. A., Romero-González. R., Martínez-Vidal, J.L., Plaza-Bolaños. P., Cuadros-Rodríguez. L.,
491   Herrera-Abdo. M.A.: Characterization of recovery profiles using gas chromatography-triple quadrupole mass
492   spectrometry for the determination of pesticide residues in meat samples, Journal. of Chromatography. A., 1133,
493   315–321 doi:10.1016/j.chroma.2006.08.039, 2006.

494   Gao, Y., Ji, H.: Characteristics of polycyclic aromatic hydrocarbons components in fine particle during heavy
495   polluting phase of each season in urban Beijing, Chemosphere., 212, 346-357,
496   doi:10.1016/j.chemosphere.2018.08.079, 2018.

497   Hester, R.E., Harrison, R. M., Larsen J.C., Larsen P.B.: Air Pollution and Health, Chapter Chemical carcinogens,
498   Royal. Society. of Chemistry., 33–56, doi:10.1039/9781847550095, 1998.

499   Hamra, G. B., Guha, N., Cohen, A., Laden, F., et al.: Outdoor particulate matter exposure and lung cancer: a
500   systematic review and meta-analysis, Environ. Health. Perspect., 122, 906–911, doi:10.1289/ehp.1408092, 2014.

501   Hannigan, M.P., Cass, G.R., Penman, B.W., Crespi, C.L., Lafleur, A.L., Busby, J. W., et al.: Bioassay-directed
502   chemical analysis of los angeles airborne particulate matter using a human cell mutagenicity assay, Environ. Sci.
503   Technol., 32, 3502–14, 1998.

504   Jia, Y., Stone, D., Wang, W., Schrlau, J., Tao, S., Simonich, SL.: Estimated reduction in cancer risk due to PAH
505   exposures if source control measures during the 2008 Beijing Olympics were sustained, Environ. Health.
506   Perspect., 119, 815–20, 2011.

507   Jakober C.A., Riddle, S.G., Robert, M.A., Destaillats, H., Charles, M.J., Green, P.G., Kleeman, M.J.: Quinone
508   Emissions from Gasoline and Diesel Motor Vehicles, Environ. Sci. Technol., 41, 4548–54,
509   doi:10.1021/es062967u, 2007.

510   Jariyasopit, N., McIntosh, M., Zimmermann, K., Arey, J., Atkinson, R., et al.: Novel Nitro-PAH Formation from
511   Heterogeneous Reactions of PAHs with NO_2, NO_3/N_2O_5, and OH Radicals: Prediction, Laboratory Studies, and
512   Mutagenicity, Environ. Sci. Technol., 48, 412–419, doi:10.1021/es4043808, 2014.

513   Janhäll, S., M. Jonsson, Å., Molnár, P., A. Svensson, E.; Hallquist, M.: Size resolved traffic emission factors of
514   submicrometer particles, Atmospheric. Environment., 38, 4331–4340, doi:10.1016/j.atmosenv.2004.04.018,
515   2004.

516   Kim, K. H., Jahan, S. A., Kabir, E., Brown, R. J. C.: A review of airborne polycyclic aromatic hydrocarbons
517   (PAHs) and their human health effects, Environment International., 60, 71–80, doi:10.1016/j.envint.2013.07.019,
518   2013.

519   Keyte, I. J., Harrison, R. M., Lammel, G.: Chemical reactivity and long-range transport potential of polycyclic
520   aromatic hydrocarbons – a review, Chem. Soc. Rev., 42, 9333 – 9391, doi:10.1039/C3CS60147A, 2013.

521   Lin, Y., Zou, J., Yang, W., Li, C.Q.: A Review of Recent Advances in Research on $PM_{2.5}$ in China, Int. J. Environ.
522   Res. Public. Health., 15, 438, doi:10.3390/ijerph15030438, 2018.

523   Liu, J., Man, R., Ma, S., Li, J., Wu, Q., Peng, J.: Atmospheric levels and health risk of polycyclic aromatic
524   hydrocarbons (PAHs) bound to $PM_{2.5}$ in Guangzhou, China, Marine. Pollution. Bulletin. 100, 134-143,
525   doi:10.1016/j.marpolbul.2015.09.014, 2015.

526   Liu, Y., Tao, S., Yang, Y., Dou, H., Yang, Y., Coveney, R.M.: Inhalation exposure of traffic police officers to
527   polycyclic aromatic hydrocarbons (PAHs) during the winter in Beijing, China, Science. of the Total.
528   Environment., 383, 98 –105, doi:10.1016/j.scitotenv.2007.05.008, 2007.

529   Liu, F., Beirle, S., Zhang, Q., Dörner, S., He, K., Wagner, T.: NOx lifetimes and emissions of cities and power
530   plants in polluted background estimated by satellite observations, Atmos. Chem. Phys., 16, 5283–5298,
531   doi:10.5194/acp-16-5283-2016, 2016.

532   Lee, C., Martin, Randal., Donkelaar, A. V., Lee, H., et al.: SO_2 emissions and lifetimes: Estimates from inverse
533   modeling using in situ and global, space-based (SCIAMACHY and OMI) observations, J. Geophys. Res., 116,
534   D06304, doi:10.1029/2010JD014758, 2011.

535   Marr, L.C., Grogan, L.A., Wöhrnschimmel, H., Molina, L.T., Molina, M.J.: Vehicle Traffic as a Source of
536   Particulate Polycyclic Aromatic Hydrocarbon Exposure in the Mexico City Metropolitan Area, Environ. Sci.
537   Technol., 38, 2584–2592, doi: 10.1021/es034962s, 2004.

538   Ministry of Ecology and Environment The People's Republic of China. Ambient air quality standards (GB-3095-
539   2012),
540   http://english.mee.gov.cn/Resources/standards/Air_Environment/quality_standard1/201605/t20160511_337502.
541   shtml

542   Niu, X., Ho, S. S. H., Ho, K. F., Huang, Y., Sun, J., Wang, Q., et al.: Atmospheric levels and cytotoxicity of
543   polycyclic aromatic hydrocarbons and oxygenated-PAHs in $PM_{2.5}$ in the Beijing-Tianjin-Hebei region,
544   Environmental. Pollution., 231, 1075-1084, doi: 10.1016/j.envpol.2017.08.099, 2017.

545   Nyiri, Z., Novák, M., Bodai, Z., Szabó, B. S., Ekea, Z., Zárayc, G., Szigeti, T.: Determination of particulate phase
546   polycyclic aromatic hydrocarbons and their nitrated and oxygenated derivatives using gas chromatography–mass
547   spectrometry and liquid chromatography–tandem mass spectrometry, Journal. of Chromatography. A., 1472, 88–
548   98, doi: 10.1016/j.chroma.2016.10.021, 2016.

549   Nisbet, I.C.T., LaGoy, P.K.: Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs),
550   Regul.   Toxicol. Pharmacol., 16, 290–300, doi:10.1016/0273-2300(92)90009-X, 1992.

551   Office of Environmental Health Hazard Assessment (OEHHA).: Benzo[a]pyrene as a Toxic Air Contaminant.
552   Available from: https://oehha.ca.gov/media/downloads/air/document/benzo5ba5dpyrene.pdf, 1994.

553   Office of Environmental Health Hazard Assessment (OEHHA).: Air Toxics Hot Spots Program Risk Assessment
554   Guidelines. Part II: Technical Support Document for Describing Available Cancer Potency Factors. Office of
555   Environmental Health Hazard Assessment. https://oehha.ca.gov/media/downloads/crnr/tsdnov2002.pdf, 105-109,
556   2002.

Atmospheric
Chemistry
and Physics
Discussions

557   Office of Environmental Health Hazard Assessment (OEHHA).: Air Toxics Hot Spots Program Risk Assessment

558   Guidelines. Part II: Technical Support Document for Describing Available Cancer Potency Factors. Office of

559   Environmental Health Hazard Assessment. https://oehha.ca.gov/media/downloads/crnr/may2005hotspots.pdf, (8

560   and A1), 2005.

561   Pio, C.A., Alves, C.A., Duarte, A.C.: Identification, abundance and origin of atmospheric organic particulate

562   matter in a Portuguese rural area, Atmos. Environ., 35, 1365–1375, https://doi.org/10.1016/S1352-

563   2310(00)00391-5, 2001.

564   Pietrogrande, M. C., Abbaszade, G., Schnelle-Kreis, J., Bacco, D., Mercuriali, M., Zimmermann, R.: Seasonal

565   variation and source estimation of organic compounds in urban aerosol of Augsburg, Germany, Environmental.

566   Pollution., 159, 1861-1868, doi:10.1016/j.envpol.2011.03.023, 2011.

567   Peng, L., Zhao, C., Lin, Y., Zheng, X., Tie, X., Chan, L. Y.: Analysis of carbon monoxide budget in North China.

568   Chemosphere. 66, 1383–1389, doi:10.1016/j.chemosphere.2006.09.055, 2007.

569   Purohit, V., Basu, A. K.: Mutagenicity of Nitroaromatic Compounds, Chem. Res. Toxicol., 13, 673−692, 2000.

570   Poulain, L., Iinuma, Y., Müller, K., Birmili, W., et al.: Diurnal variations of ambient particulate wood burning

571   emissions and their contribution to the concentration of Polycyclic Aromatic Hydrocarbons (PAHs) in Seiffen,

572   Germany, Atmos. Chem. Phys., 11, 12697-12713, doi:10.5194/acp-11-12697-2011, 2011.

573   Ramírez, N., Vallecillos, L., Lewis, A.C., Borrull, F., Marcé, R. M., Hamilton, J. F.: Comparative study of

574   comprehensive gas chromatography-nitrogen chemiluminescence detection and gas chromatography-ion trap-

575   tandem mass spectrometry for determining nicotine and carcinogen organic nitrogen compounds in thirdhand

576   tobacco smoke, Journal. of Chromatography. A., 1426, 191–200, doi:10.1016/j.chroma.2015.11.035, 2015.

577   Ramírez, N., Cuadras, A., Rovira, Enric., Marcé, R.M., Borrull, F.: Risk Assessment Related to Atmospheric

578   Polycyclic Aromatic Hydrocarbons in Gas and Particle Phases near Industrial Sites, Environmental. Health.

579   Perspectives., 119, doi:10.1289/ehp.1002855, 2011.

580   Raaschou-Nielsen, O., Andersen, N.Z., Beelen, R., et al.: Air pollution and lung cancer incidence in 17 European

581   cohorts: prospective analyses from the European Study of Cohorts for Air Pollution Effects (ESCAPE), Lancet.

582   Oncol., 14, 813–822, doi: 10.1016/S1470-2045(13)70279-1, 2013.

583   Ringuet, J., Albinet, A., Leoz-Garziandia, E., Budzinski, H., Villenave, E.: Diurnal/nocturnal concentrations and

584   sources of particulate-bound PAHs, OPAHs and NPAHs at traffic and suburban sites in the region of Paris

585   (France), Science. of the Total. Environment., 437, 297–305, doi.org/10.1016/j.scitotenv.2012.07.072, 2012.

586   Riva, M., Healy, R.M., Flaud, P.M., Perraudin, E., Wenger, J.C., Villenave, E.: Gas- and Particle-Phase Products

587   from the Chlorine-Initiated Oxidation of Polycyclic Aromatic Hydrocarbons, *J. Phys. Chem. A*., 119, 11170-

588   11181, doi:10.1021/acs.jpca.5b04610, 2015.

589   Ramdahl, T., Zielinska, B., Arey, J., Atkinson, R., Winer, A. M., Pitts Jr, J. N.: Ubiquitous occurrence of 2-

590   nitrofluoranthene and 2-nitropyrene in air, Nature., 321, 425-427, 1986.

Atmospheric
Chemistry
and Physics
Discussions

591   Shen, G., Tao, S., Wei, S., Zhang, Y., Wang, R., Wang, B., et al.: Emissions of parent, nitro, and oxygenated

592   polycyclic aromatic hydrocarbons from residential wood combustion in rural China, Environ. Sci. Technol., 46,

593   8123–30, doi:10.1021/es301146v, 2012.

594   Sasaki, J., Aschmann, SM., Kwok, E.S.C., Atkinson, R., Arey, J.: Products of the gas-phase OH and NO_3 radical-

595   initiated reactions of naphthalene, Environ. Sci. Technol., 31, 3173–9, 1997.

596   Saikawa, E., Naik, V., Horowitz, L. W., Liu, J. F., Mauzerall, D. L.: Present and potential future contributions of

597   sulfate, black and organic carbon aerosols from China to global air quality, premature mortality and radiative

598   forcing, Atmos. Environ., 43, 2814–2822, doi:10.1016/j.atmosenv.2009.02.017, 2009.

599   Sharma, H., Jain, V.K., Khan, Z.H.: Characterization and source identification of polycyclic aromatic

600   hydrocarbons (PAHs) in the urban environment of Delhi, Chemosphere., 66, 302–310,

601   doi:10.1016/j.chemosphere.2006.05.003, 2007.

602   Song, H., Zhang, Y., Luo, M., Gu, J., Wu, M., Xu, D., Xu, G., Ma, L.: Seasonal variation, sources and health risk

603   assessment of polycyclic aromatic hydrocarbons in different particle fractions of $PM_{2.5}$ in Beijing, China,

604   Atmospheric Pollution Research., 10, 105-114, doi:10.1016/j.apr.2018.06.012, 2019.

605   Tobiszewski, M., Namieśnik, J.: PAH diagnostic ratios for the identification of pollution emission sources,

606   Environmental. Pollution., 162, 110-119, doi:10.1016/j.envpol.2011.10.025, 2012.

607   Tsapakis, M. and Stephanou, E. G. Collection of gas and particle semi-volatile organic compounds: use of an

608   oxidant denuder to minimize polycyclic aromatic hydrocarbons degradation during high-volume air sampling,

609   Atmos. Environ., 37, 4935–4944, doi:10.1016/j.atmosenv.2003.08.026, 2003.

610   Tsapakis, M., and Stephanou, E. G: Diurnal Cycle of PAHs, Nitro-PAHs, and oxy-PAHs in a High Oxidation

611   Capacity Marine Background Atmosphere, Environ. Sci. Technol., *41,* 8011–8017, doi: 10.1021/es071160e,

612   2007.

613   Tian,Y., Xiao,Z., Wang, H., et al.: Influence of the sampling period and time resolution on the PM source

614   apportionment: Study based on the high time-resolution data and long-term daily data, Atmos. Environ., 165, 301-

615   309, doi:10.1016/j.atmosenv.2017.07.003, 2017.

616   World Health Organization (WHO), outdoor air pollution, IARC Monographs on the Evaluation of Carcinogenic

617   Risks to Humans, International Agency for Research on Cancer., 109, 2016.

618   World Health Organization (WHO), Air Quality Guidelines for Europe. 2nd ed. Copenhagen: WHO, Regional

619   Office for Europe (Copenhagen). http://www.euro.who.int/__data/assets/pdf_file/0005/74732/E71922.pdf,

620   Chapter 5, 92 – 94, 2000.

621   Wenyuan, Chen., and Tong Zhu.: Formation of Nitroanthracene and Anthraquinone from the Heterogeneous

622   Reaction Between NO_2 and Anthracene Adsorbed on NaCl Particles, Environ. Sci. Technol., 48, 8671–8678,

623   doi:10.1021/es501543g, 2014.

624   Wang, G., Kawamura, K., Lee, S., Ho, K., Cao, J.: Molecular, Seasonal, and Spatial Distributions of Organic

625   Aerosols from Fourteen Chinese Cities, Environ. Sci. Technol., 40, 4619-4625, doi:10.1021/es060291x, 2006.

Atmospheric
Chemistry
and Physics
Discussions

Open Access

626   Wang, W., Jariyasopit, N., Schrlau, J., Jia, Y., Tao, S., Yu, T.W., et al.: Concentration and Photochemistry of
627   PAHs, NPAHs, and OPAHs and Toxicity of $PM_{2.5}$ during the Beijing Olympic Games, Environ. Sci. Technol.,
628   45, 6887–95, doi:10.1021/es201443z, 2011a.

629   Wang, W., Huang, M.J., Kang, Y., Wang, H.S., Leung, A.O.W., Cheung, K.C., Wong, M.H.: Polycyclic aromatic
630   hydrocarbons (PAHs) in urban surface dust of Guangzhou, China: Status, sources and human health risk
631   assessment, Science. of the Total. Environment., 409, 4519–4527, doi:10.1016/j.scitotenv.2011.07.030, 2011b.

632   Wei, C., Bandowe, B.A.M., Han Y., Cao, J., Zhan, C., Wilcke, W.: Polycyclic aromatic hydrocarbons (PAHs)
633   and their derivatives (alkyl-PAHs, oxygenated-PAHs, nitrated-PAHs and azaarenes) in urban road dusts from
634   Xi'an, Central China, Chemosphere., 134, 512-520, doi:10.1016/j.chemosphere.2014.11.052, 2015.

635   Wang, W., Simonich, S.L.M., Wang, W., Giri, B., Zhao, J., Xue, M., Cao, J., Lu, X., Tao, S.: Atmospheric
636   polycyclic aromatic hydrocarbon concentrations and gas/particle partitioning at background, rural village and
637   urban sites in the North China Plain, Atmospheric. Research., 99, 197–206, doi:10.1016/j.atmosres.2010.10.002,
638   2011C.

639   Wu, Y., Yang, L., Zheng, X., Zhang, S., Song, S., Li, J., Hao, J.: Characterization and source apportionment of
640   particulate PAHs in the roadside environment in Beijing, Science of the Total Environment 470-471, 76-83, doi:
641   10.1016/j.scitotenv.2013.09.066, 2014.

642   Xu, S.S., Liu, W.X., Tao, S.: Emission of polycyclic aromatic hydrocarbons in China, Environ. Sci. Technol., 40,
643   702–708, doi:10.1021/es0517062, 2006.

644   Yunker, M.B., Macdonald, R.W., Vingarzanc, R., Mitchell, R.H., Goyette, D., Sylvestre, S.: PAHs in the Fraser
645   River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition, Org. Geochem., 33,
646   489–515, doi:10.1016/S0146-6380(02)00002-5, 2002.

647   Zimmermann, K., Jariyasopit, N., Massey Simonich, S. L., Tao, S., Atkinson, R., Arey, J.: Formation of Nitro-
648   PAHs from the Heterogeneous Reaction of Ambient Particle-Bound PAHs with $N_2O_5/NO_3/NO_2$, Environ. Sci.
649   Technol., 47, 8434−8442, doi:10.1021/es401789x, 2013.

650   Zhang, Y. X., Tao, S.: Global atmospheric emission inventory of polycyclic aromatic hydrocarbons (PAHs) for
651   2004, Atmos. Environ., 43, 812–819, doi:10.1016/j.atmosenv.2008.10.050, 2009.

652   Zhang, J., Yang, L., Mellouki, A., Chen, J., Chen, X., Gao, Y., Jiang, P., Li, Y., Yu, H., Wang, W.: Atmospheric
653   PAHs, NPAHs, and OPAHs at an urban, mountainous, and marine sites in Northern China: Molecular
654   composition, sources, and ageing, Atmos. Environ., 173, 256–264, doi:10.1016/j.atmosenv.2017.11.002, 2018.

655   Zhang, W., Tong, S., Ge, M., An, J., Shi, Z., Hou, S., Xia, K., Qu, Y., Zhang, H., Chu, B., Sun, Y., He, H.:
656   Variations and sources of nitrous acid (HONO) during a severe pollution episode in Beijing in winter 2016,
657   Science. of the Total. Environment., 648, 253–262, doi: 10.1016/j.scitotenv.2018.08.133, 2019.

658

659

660

661
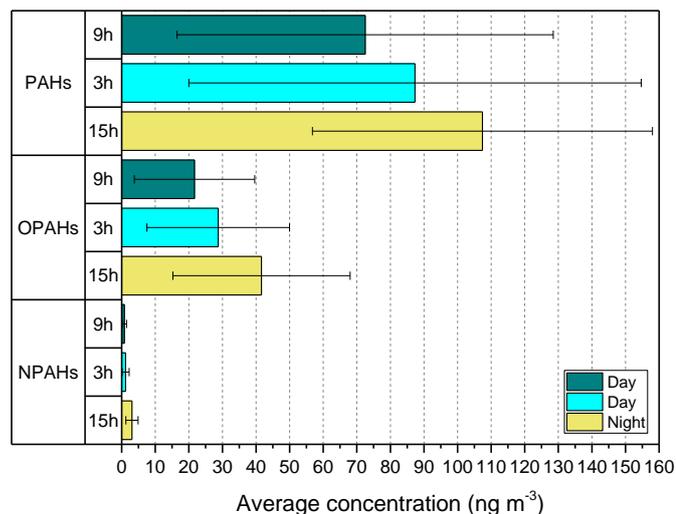
Figure 1. Average distribution diagram of ∑PAHs, ∑OPAHs and ∑NPAHs in PM$_{2.5}$ samples during the daytime (1/3 h; 1/9 h) and night-time (1/15 h). Error bars reflect standard deviations.

664

665

666

Table 1. List of measured PAHs, OPAHs and NPAHs and their Abbreviations. Compounds are listed in order of elution.

| Compound/Formula	Abbreviation	Accurate Mass (*m/z*)	%RSD	
16 PAHs		Monitored ions in EI mode	Interday	Intraday
Naphthalene/C$_{10}$H$_8$	NAP	128.0628-127.0543-102.0464	4.6	3.2
Acenaphthylene/C$_{12}$H$_8$	ACY	152.0629-151.0546-126.0463	4.1	2.1
Acenaphthene/ C$_{12}$H$_{10}$	AC	153.0705-154.0779-152.0634	5.5	6.1
Fluorene/ C$_{13}$H$_{10}$	FLU	166.0782-165.0708-164.0621	4.0	2.9
Phenanthrene/C$_{14}$H$_{10}$	PHE	178.0789-176.0626-152.0622	4.6	3.0
Anthracene/C$_{14}$H$_{10}$	ANT	178.0787-176.0627-152.0620	4.7	4.2
Fluoranthene/C$_{16}$H$_{10}$	FLT	202.0788-200.0626-101.0388	1.8	4.5
Pyrene/C$_{16}$H$_{10}$	PYR	202.0788-200.0626-101.0389	3.2	1.9
Benzo[a]anthracene/C$_{18}$H$_{12}$	BaA	228.0927-226.0783-101.0388	6.2	1.2
Chrysene/C$_{18}$H$_{12}$	CHR	228.0943-226.0784-101.0387	6.0	2.6
Benzo[b]fluoranthene/C$_{20}$H$_{12}$	BbF	252.0941-250.0784-126.0467	4.7	2.0

667
668

Atmospheric
Chemistry
and Physics
Discussions

Benzo[k]fluoranthene/$C_{20}H_{12}$	BkF	252.0940-250.0783-126.0468	8.9	8.7
Benzo[a]pyrene/$C_{20}H_{12}$	BaP	252.0940-250.0783-126.0466	5.2	2.3
Indeno[1,2,3-cd]pyrene/$C_{22}H_{12}$	IcdP	276.0939-274.0783-138.0467	7.2	2.6
Dibenz[a,h]anthracene/$C_{22}H_{14}$	DahA	278.1097-276.0941-139.0545	7.7	4.3
Benzo[ghi]perylene/$C_{22}H_{12}$	BghiP	276.0942-274.0783-138.0467	5.4	2.6
10 OPAHs		Monitored ions in NCI mode		
1,4-Naphtoquinone/$C_{10}H_6O_2$	1,4-NAQ	158.0420	6.3	5.1
1-Naphthaldehyde/$C_{11}H_8O$	1-NALD	156.0557	8.9	7.8
9-Fluorenone/$C_{13}H_8O$	9-FLON	180.0639	5.7	6.2
9,10-Anthraquinone/$C_{14}H_8O_2$	9,10-ANQ	208.0572	5.6	3.2
1,8-Naphthalic anhydride/ $C_{12}H_6O_3$	1,8-NANY	198.0436	6.4	5.6
Phenanthrene-9-carboxaldehyde/$C_{15}H_{10}O$	PHCA	206.0777	5.4	4.9
Benzo[a]fluorenone/ $C_{17}H_{10}O$	BaFLU	230.0791	6.4	3.2
7H-Benz[de]anthracene-7-one/ $C_{17}H_{10}O$	BANTone	230.0781	7.2	5.8
1-Pyrenecaboxaldehyde/ $C_{17}H_{10}O$	1-PYRCA	230.0786	7.5	7.2
1,2-Benzanthraquinone/ $C_{18}H_{10}O_2$	1,2-BANQ	258.0743	8.5	7.4
9 NPAHs		Monitored ions in NCI mode		
1-Nitronaphthalene/$C_{10}H_7NO_2$	1-NNAP	173.0551	4.7	4.4
3-Nitrodibenzofuran/ $C_{12}H_7NO_3$	3-NDBF	213.0475	4.4	5.1
5-Nitroacenaphthene/ $C_{12}H_9NO_2$	5-NAC	199.0682	5.6	5.3
2-Nitrofluorene/$C_{13}H_9NO_2$	2-NFLU	211.0689	5.0	5.4
9-Nitroanthracene/$C_{14}H_9NO_2$	9-NANT	223.0697	5.9	3.9
3-Nitrofluoranthene/$C_{16}H_9NO_2$	3-NFLT	247.0688	6.4	4.1
1-Nitropyrene/$C_{16}H_9NO_2$	1-NPYR	247.0691	3.9	3.2
6-Nitrochrysene/$C_{18}H_{11}NO_2$	6-NCHR	273.0847	4.7	5.4
6-Nitrobenzo[a]pyerene/ $C_{20}H_{11}NO_2$	6-NBaP	297.0845	8.4	9.7

669
670

671
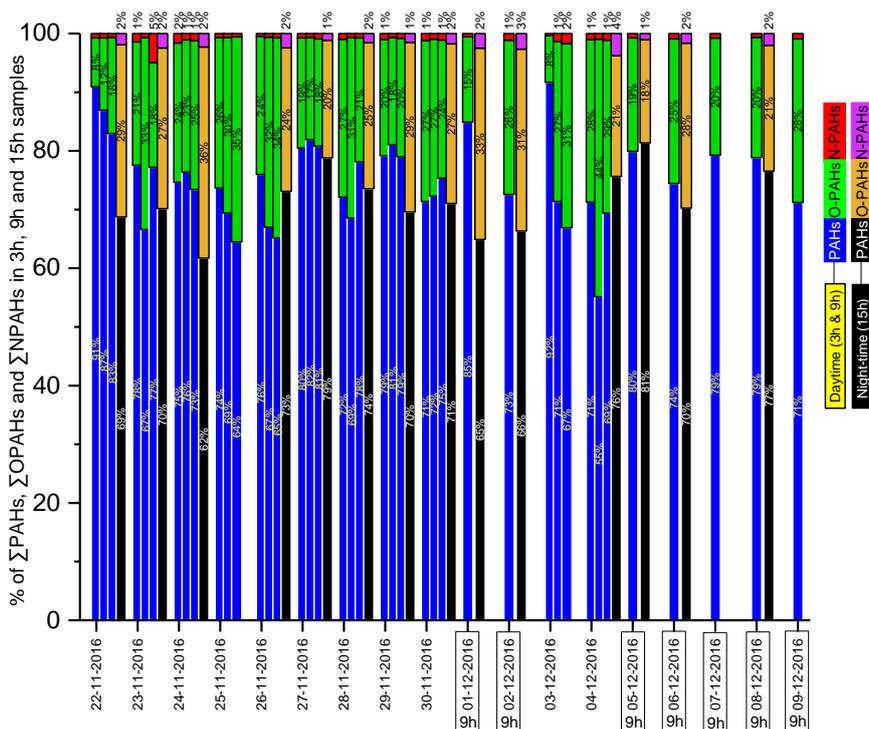
Figure 2. Temporal profile of ∑PAHs, ∑OPAHs and ∑NPAHs in PM$_{2.5}$ samples during the daytime and night-time.

Percentage below 1% for NPAHs are omitted for clarity.

674

675

676

Atmospheric
Chemistry
and Physics
Discussions

677

678

679

680   **Table 2. Minimum, maximum and average atmospheric concentrations of PAHs, OPAHs and NPAHs in PM$_{2.5}$.**

681   **Compounds in bold represent the highest mean contribution to the sum of all compounds.**

Compound	Concentrations (ng m^{-3})		Average contribution
	Minimum-maximum	Average	to total (%)
16 PAHs	(3 h)/(9 h)/(15 h)	(3 h)/(9 h)/(15 h)	(3 h)/(9 h)/(15 h)
NAP	(0.05-0.8)/(0.1-0.4)/(0.06-0.6)	(0.31)/(0.24)/(0.27)	(0.48)/(0.39)/(0.25)
ACY	(0.01-1.2)/(0.1-0.8)/(0.1-1.2)	(0.31)/(0.31)/(0.58)	(0.35)/(0.46)/(0.50)
AC	(0.03-0.13)/(0.02-0.09)/(0.01-0.2)	(0.07)/(0.04)/(0.07)	(0.15)/(0.08)/(0.06)
FLU	(0.05-1.3)/(0.1-1.0)/(0.1-1.5)	(0.43)/(0.41)/(0.63)	(0.53)/(0.65)/(0.56)
PHE	**(1.2-23.1)/(1.9-16.3)/(1.5-13.7)**	**(7.38)/(6.30)/(8.40)**	**(8.83)/(9.04)/(7.84)**
ANT	(0.5-3.4)/(0.3-1.9)/(0.3-2.9)	(1.07)/(0.79)/(1.43)	(1.48)/(1.23)/(1.32)
FLT	**(1.4-41.8)/(3.0-17.6)/(3.2-11.7)**	**(12.86)/(9.10)/(8.97)**	**(13.93)/(13.96)/(9.67)**
PYR	**(0.7-34.6)/(2.1-15.7)/(2.9-10.7)**	**(9.85)/(7.48)/(8.09)**	**(10.36)/(11.04)/(8.69)**
BaA	**(1.3-27.7)/(1.3-17.5)/(2.1-18.8)**	**(6.69)/(6.52)/(12.03)**	**(7.17)/(8.23)/(11.04)**
CHR	**(1.4-37.5)/(2.1-20.8)/(2.7-15.9)**	**(10.49)/(9.17)/(11.27)**	**(11.23)/(12.38)/(10.78)**
BbF	**(1.5-35.3)/(2.1-21.3)/(2.3-20.4)**	**(10.34)/(8.93)/(10.79)**	**(11.19)/(11.76)/(10.42)**
BkF	(1.6-15.4)/(1.2-7.4)/(1.3-6.6)	(5.51)/(3.94)/(4.30)	(6.76)/(5.80)/(4.43)
BaP	**(1.4-37.3)/(1.5-20.7)/(3.2-35.2)**	**(8.81)/(8.40)/(18.91)**	**(9.12)/(10.28)/(16.15)**
IcdP	(1.7-16.1)/(0.9-11.6)/(1.0-18.3)	(4.79)/(4.65)/(9.75)	(6.06)/(5.70)/(8.03)
DahA	(1.9-5.2)/(0.7-2.9)/(0.5-6.9)	(2.54)/(1.46)/(3.02)	(4.43)/(2.46)/(2.56)
BghiP	(2.53-17.0)/(1.2-10.7)/(1.4-15.4)	(5.80)/(4.70)/(8.80)	(7.86)/(6.47)/(7.62)
Total	(18-297)/(19-167)/(23-165)	(87.32)/(72.5)/(107.40)	
10 OPAHs	(3 h)/(9 h)/(15 h)	(3 h)/(9 h)/(15 h)	(3 h)/(9 h)/(15 h)
1,4-NAQ	(0.02-8.1)/(0.16-3.1)/(0.1-4.2)	(2.25)/(1.27)/(1.66)	(6.22)/(5.39)/(3.70)
1-NALD	(0.2-0.8)/(0.07-0.5)/(0.08-0.9)	(0.43)/(0.20)/(0.49)	(2.71)/(1.19)/(1.25)
9-FLON	**(0.49-14.9)/(0.7-6.0)/(0.8-11.4)**	**(6.76)/(2.56)/(4.26)**	**(25.84)/(14.30)/(10.25)**
9,10-ANQ	**(0.3-36.4)/(1.2-46.1)/(2.8-36.04)**	**(8.31)/(13.33)/(14.28)**	**(24.31)/(35.83)/(32.74)**
1,8-NANY[a]	**(0.3-16.3)/(1.0-6.9)/(3.7-9.3)**	**(7.09)/(3.69)/(6.81)**	**(37.86)/(33.25)/(45.64)**
PHCA	(0.1-0.9)/(0.05-0.6)/(0.06-1.9)	(0.26)/(0.20)/(0.71)	(1.42)/(0.99)/(1.50)
BaFLU	(0.06-10.8)/(0.1-8.1)/(0.4-15.1)	(2.77)/(2.72)/(5.99)	(7.47)/(9.73)/(12.07)
BANTone	(0.08-15.1)/(0.04-8.3)/(0.5-19.8)	(2.46)/(2.63)/(9.27)	(6.10)/(9.05)/(19.12)
1-PYRCA	(0.007-1.8)/(0.008-1.5)/(0.05-4.2)	(0.31)/(0.39)/(1.31)	(0.74)/(1.24)/(1.96)

Atmospheric
Chemistry
and Physics
Discussions

1,2-BANQ	(0.02-3.6)/(0.03-2.6)/(0.2-10.3)	(0.87)/(0.90)/(2.77)	(2.3)/(3.24)/(4.33)
Total	(1.8-87.9)/(3.6-55.3)(8.9-95.5)	(28.74)/(21.68)/(41.63)	
9 NPAHs	(3 h)/(9 h)/(15 h)	(3 h)/(9 h)/(15 h)	(3 h)/(9 h)/(15 h)
1-NNAP	(0.01-0.1)/(0.008-0.04)/(0.005-0.03)	(0.03)/(0.01)/(0.01)	(4.38)/(3.08)/(0.57)
3-NDBF	**(0.08-1.5)/(0.02-0.06)/(0.03-2.4)**	**(0.33)/(0.03)/(0.89)**	**(33.39)/(7.92)/(22.39)**
5-NAC[b]	(0.04-0.1)/(<LOQ)/(0.03-0.35)	(0.08)/(<LOQ)/(0.18)	(5.64)/(<LOQ)/(4.67)
2-NFLU	(0.03-0.3)/(0.01-0.3)/(0.01-0.5)	(0.08)/(0.09)/(0.26)	(10.15)/(10.00)/(7.28)
9-NANT	**(0.01-1.2)/(0.06-0.1)/(0.4-2.4)**	**(0.36)/(0.41)/(1.18)**	**(27.13)/(53.45)/(47.5)**
3-NFLT	**(0.05-1.2)/(0.02-0.5)/(0.04-1.2)**	**(0.34)/(0.21)/(0.54)**	**(24.56)/(23.45)/(17.67)**
1-NPYR[c]	(0.01-0.1)/(0.01-0.06)/(0.008-0.2)	(0.05)/(0.06)/(0.02)	(2.92)/(2.48)/(2.01)
6-NCHR[d]	(0.05-0.2)/(<LOQ)/(0.009-0.02)	(0.09)/(<LOQ)/(0.01)	(5.6)/(<LOQ)/(0.5)
6-NBaP[e]	(<LOQ)/(<LOQ)/(0.02-0.08)	(<LOQ)/(<LOQ)/(0.05)	(<LOQ)/(<LOQ)/(1.26)
Total	(0.15-3.92)/(0.13-2.0)/(0.57-6.43)	(1.17)/(0.80)/(3.06)	

682 [a] Quantified in 28/54 samples
683 [b] Quantified in 7/54 samples
684 [c] Quantified in 35/54 samples
685 [d] Quantified in 5/54 samples
686 [e] Quantified in 11/54 samples
687 [NA] Not available due to lack of data for 3 h samples.
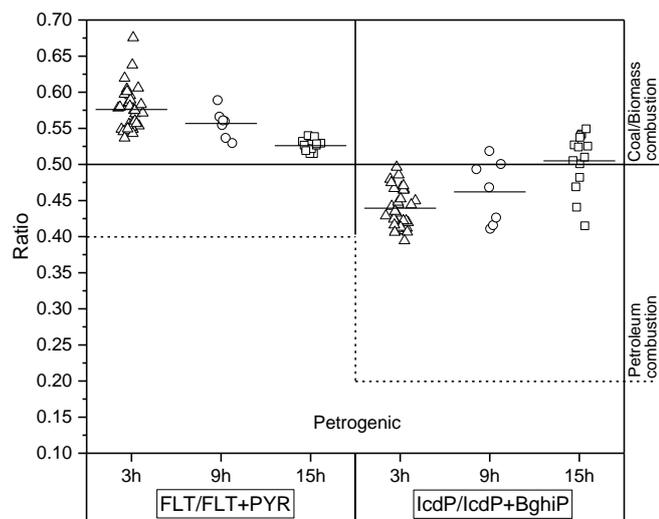
688

689

690

691

692

Figure 3. Column scatter of FLT/(FLT + PYR) and IcdP/(IcdP + BghiP) in the particulate phase at three different time

sampling, open triangles and circles represent the daytime data for 3 h and 9 h samples, respectively, open squares

represent the night-time data of 15 h. The dash line separates the petroleum combustion source from petrogenic source

for both ratios. The solid short line on each data set represent the mean value of ratios.

697

698

Table 3. Average Concentration of $\sum BaP_{eq}$ in ng m^{-3} and cancer risk assessment for the sum of 16PAHs, 1OPAH and

6NPAHs.

Sampling hours	$\sum[BaP]_{eq}$ ng m^{-3}	$UR_{BaP} = 1.1x10^{-6}$ (CalEPA)	$UR_{BaP} = 8.7x10^{-5}$ (WHO)	Risk per million people
9 h (daytime, n=40)[a]	15.9[a]	1.75 x 10^{-5}	1.38 x 10^{-3}	17[b] – 1383[c]
15 h (night-time, n=14)	28.28	3.17 x 10^{-5}	2.46 x 10^{-3}	31[b] – 2460[c]
24h (n=54)	**23.6**	**2.6 x 10^{-5}**	**2.05 x 10^{-3}**	**26[b] – 2053[c]**

[a] Average includes combined 3 h samples in each day (n=33) and 9 h samples (n=7)
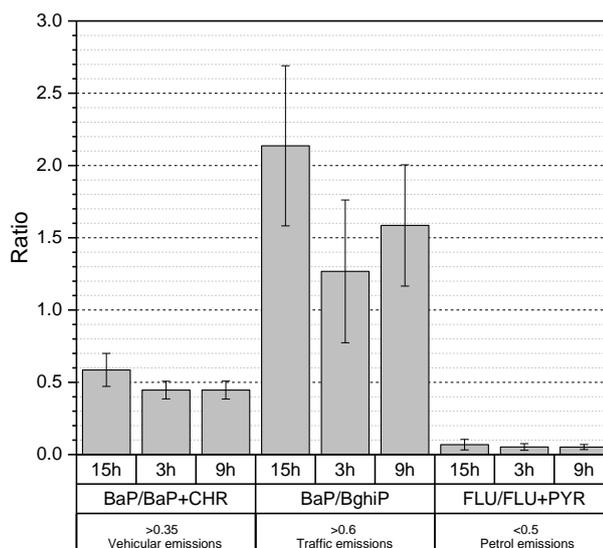[b] Calculated Value according to CalEPA
[c] Calculated Value according to WHO
n: number of samples

706

Figure 4. Column distribution of BaP/BaP+CHR, BaP/BghiP and FLU/FLU+PYR in the particulate phase at three different time sampling. 3 h and 9 h represent samples collected during the day and 15 h for samples at night. Error bars reflect standard deviations.

707
708
709
710
711
712
713
714
715
716
717
718
719
720
721
722
723
724
725
726

727
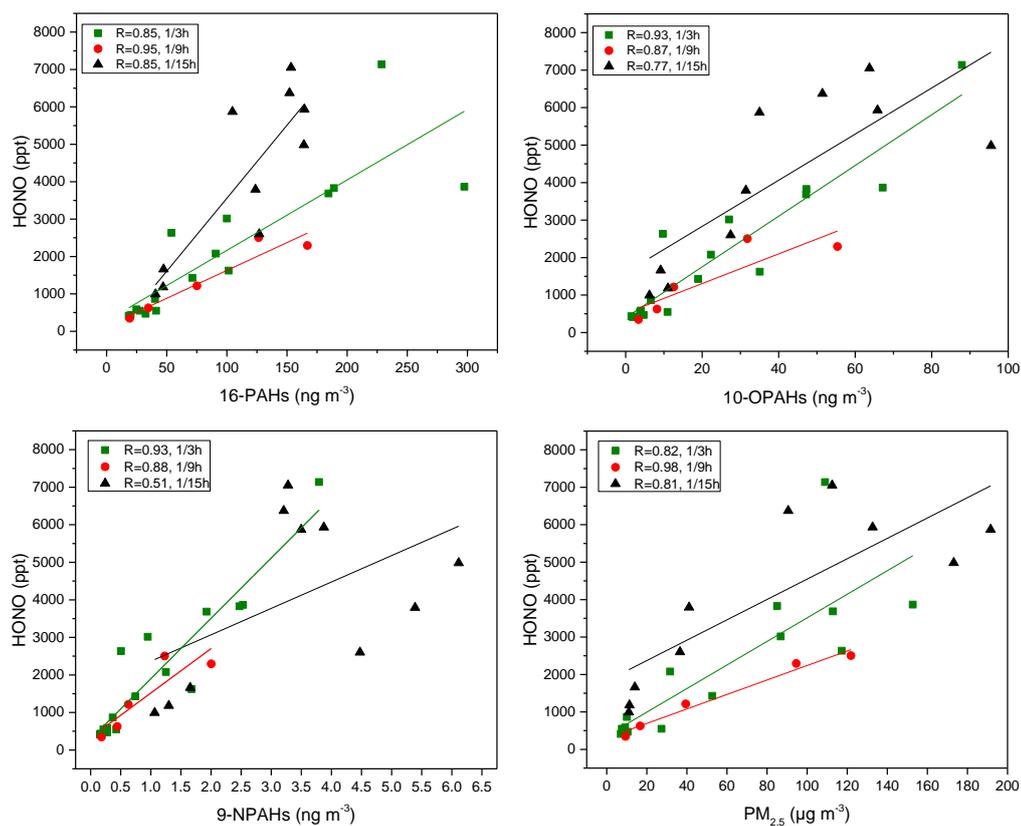
Figure 5. Correlation coefficient of ∑PAHs, ∑OPAHs, ∑NPAHs and PM$_{2.5}$ with HONO. Time sampling resolution 1/3 h and 1/9 h refer to diurnal concentrations and 1/15 h to nocturnal concentrations. Significance levels were between 0.001 and 0.05 except for HONO and NPAHs at night, P level > 0.05 and Pearson coefficient 0.52.

731

Atmospheric
Chemistry
and Physics
Discussions

732

733
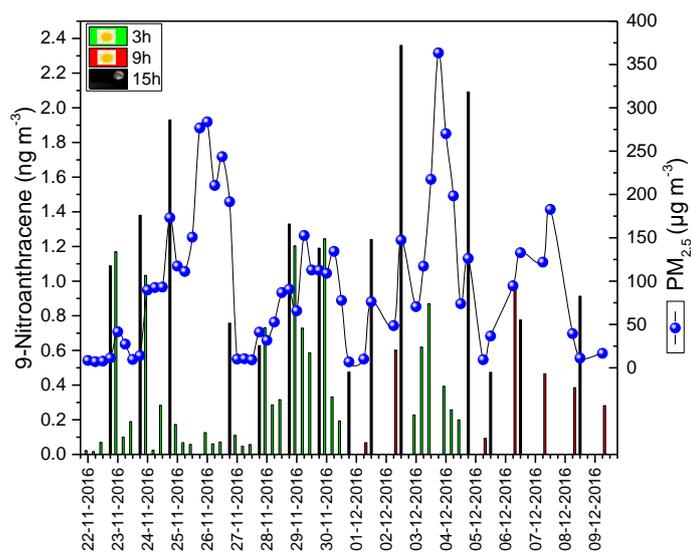
Figure 6. Temporal variation of 9-Nitroanthrance and PM$_{2.5}$ during the entire winter campaign.

735